Electroplating of TiB$_2$ in NaF-NaBF$_4$ Eutectic Melt with Titanium Fluoride

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TiB$_2$-coated metal should be a very promising material for many purposes. One of the hardest problems on TiB$_2$ coating is to prevent cracking or stripping by thermal expansion gap between TiB$_2$ deposit and substrate. In this study, we have investigated the electroplating of TiB$_2$ in NaF-NaBF$_4$ eutectic melt (m.p. 657K) with Na$_2$TiF$_6$ or TiF$_5$. The constant-potential electrolysis was carried out at various potentials. The electrodeposit was obtained at more negative potential than that of reduction of Ti(III) to Ti(II). The result of EPMA and XRD showed that the main ingredient of electrodeposit was TiB$_2$. The morphology of electrodeposit changed remarkably at the potential where the cathodic current began to increase sharply in a voltammogram. The flat and adhesive deposit was obtained at more positive potential, while the electrodeposit became powdery at more negative potential. The morphology also changed with time, that is, the protuberant deposit grew with the current increase after a certain time even at the potential where the flat deposit was expected. The monitoring of current was important for depositing the thick and flat layer in this process, and the layer up to 50µm was obtained under suitable conditions. The dependence of the morphology on Ti ion concentration or substrate was not critical in this process.

Keyword: molten salt, electroplating, TiB$_2$, NaF-NaBF$_4$, Na$_2$TiF$_6$, TiF$_5$, NaTiF$_4$

I. Introduction

Titanium diboride has the characteristics of high strength, abrasion resistance and corrosion resistance. The bulk material of TiB$_2$ was conventionally made by powder metallurgy, but it is mechanically fragile. Furthermore, this material is usually expensive because of the complicated process and the difficulty of sintering TiB$_2$ powders. If construction materials with mechanical toughness, such as steel, can be coated with TiB$_2$, the material with superior property of TiB$_2$ and substrate might be supplied at lower price.

Many methods, e.g. PVD, CVD and thermal spray, have been studied for TiB$_2$ coating process. The electroplating in a molten salt system is one of the most promising processes. The studies on TiB$_2$ electroplating in oxide melts[3,4] or alkaline metal fluorides[5,6] have been reported.

The electroplating process of TiB$_2$ should be carried out at as low temperature as possible, because the TiB$_2$ layer is cracked or stripped easily by thermal expansion gap between TiB$_2$ and electrode material. We have been investigating TiB$_2$ electroplating in NaF-NaBF$_4$ eutectic melt with Ti fluoride, which had a lower melting point (657K) than that of LiF-KF-NaF eutectic or molten oxides. We have reported the result on cathodic reactions in this melt[7].

In this paper, we discussed the dependence of ingredients and morphology of electrodeposit on the electrolytic conditions in this system, and showed the condition where a flat, dense and adhesive TiB$_2$ electrodeposit layer was obtained. The effect of the substrate on morphology was also examined. The electrolysis was carried out at a constant potential which was fixed referring to the result of voltammetry.

II. Experimental

The electrolysis was performed in a carbon crucible, which was placed in the airtight container in an Ar-filled glove box to prevent the NaF-NaBF$_4$ melt from thermal decomposition. The container was heated by an electric furnace. A NaF-NaBF$_4$ eutectic mixture was prepared by mixing NaF and NaBF$_4$ both of which had been vacuum-dried at 423K for 24h separately. After the mixture was fused in a carbon crucible, Na$_2$TiF$_6$ (Kishida chem, reagent grade) or TiF$_5$ (Cerac, 99%) was added.

An electrolytic cell is shown in Fig.1. For voltammetric investigation, the working electrode was Ni wire covered with high purity alumina sheath (active area: 1mm$\phi$×10mm). For electrolysis, the cathode was Ni or Fe plate (20mm×5mm×0.5mm). Carbon rod (4mm$\phi$×80mm) was used as a counter electrode for NaF-NaBF$_4$ without Titanium fluoride, while a Ti rod (10mm$\phi$×80mm) was used for NaF-NaBF$_4$ with Titanium fluoride. A quasi-reference electrode was the same as the working electrode for voltammetry and its potential was checked against sodium potential mentioned later. The standard potential in this paper was this sodium potential.

The measurement system was composed of a potentiationstat driven by a function generator, a couloumometer, an X-Y recorder and an X-t recorder. The melt temperature was measured by an alumel-chromel thermocouple protected by an alumina tube. The thermocouple was set outside the crucible at the same height as bath in order to prevent the alumina sheath from dissoloution to the bath.

The electrodes were polished with emery paper, rinsed with acetone and dried at 373K. The Ni plate electrode was electro-etched at +0.2V (versus the quasi-reference electrode) for a
few minutes before electrolysis. The voltammetry was carried out to check the relation between the potential and current. The constant-potential electrolysis was carried out based on the results of voltammetry. The electrodeposition on electrode was cooled at the top in cell, and was rinsed with distilled water in order to remove residual melt. The surface and cross section of electrodeposition were observed by a scanning electron microscope (SEM), and analyzed by electron probe microanalysis (EPMA) and X-ray diffraction (XRD). The current efficiency was calculated from the quantity of electricity and the electrodeposition weight.

III. Results and Discussions

1. Voltammetry

In the cathodic scan of voltammetry, regardless of the Ti ion concentration, the cathodic current began to increase sharply at much lower potential than that of boron deposition, which was confirmed in the melt without Ti ion. It was considered that this cathodic current corresponded to the sodium deposition. Because the proper reference electrode has not reported in this system, the potential of this sodium deposition was used as the standard in this paper.

The voltammograms in NaF-NaBF₄ eutectic melt with Na₂TiF₆ (0.493 mol%) and without Na₂TiF₆ were shown in Fig. 2. There were two changes in cathodic current at 1.1 V(II) and 2.0 V(III') with Ti ion addition. Change in voltammograms with scan rate with switching potential 1.2 V was shown in Fig. 3. A new cathodic current peak(II') was observed at about 1.6 V. It is considered that the cathodic current peaks(II, III') correspond to the diffusion controlled reaction of Ti ion because their values increased with an increase in scan rate and Na₂TiF₆ concentration.

The number of electron transferred by the reaction at the peak(III') was evaluated about 0.98, and the electrodeposition had not been obtained around this potential. The peak(III') corresponds to the reaction as follows;

\[ \text{Ti(IV)} + e^- \rightarrow \text{Ti(III')} \]  \hspace{1cm} (1)

The number of electron transferred by the reaction at the peak(II') was not evaluated in NaF-NaBF₄-Na₂TiF₆ system.

The cathodic peak current (II') was observed at almost the same potential of peak(II') in NaF-NaBF₄-TiF₃ system. This cathodic peak current increased with an increase in scan rate and TiF₃ concentration. The number of electron transferred by the reaction at the peak(II') was evaluated about 1.14. The cathodic current peak(II') corresponds to the reaction as follows;

\[ \text{Ti(III')} + e^- \rightarrow \text{Ti(II')} \]  \hspace{1cm} (2)

By comparison between the voltammograms measured in NaF-
NaBF₄-TiF₃ system and NaF-NaBF₄-Na₂TiF₆, the cathodic current peak(II') was considered to correspond to the reaction(2).

2. Electrodeposition

2-1. Morphology

The constant-potential electrolysis was carried out in NaF-
NaBF₄-Na₂TiF₆ system at various potentials, classified into three regions (①, ②, ③) as shown in Figs. 2 and 3. The region① is a more negative potential region than the potential (I') where

![Fig. 1 Electrolytic cell.](image)

![Fig. 2 Change in voltammogram with Na₂TiF₆ addition at 673K](image)

![Fig. 3 Change in voltammogram with scan rate with Na₂TiF₆ at 673K](image)
the cathodic current increases sharply. The region② is a potential region between the potential (I) and the cathodic current peak (II'). The region③ is a more positive potential region than the peak (II').

The SEM images of typical electrodeposits on Ni electrode were shown in Fig.4. The electrodeposits were obtained in the regions① and ②, but were not in the region③. The deposits obtained in the regions① and ② were different at some points. The color of electrodeposits obtained in the region① was black, while that in the region② was gray. The electrodeposits in the region① were dendritic or powdery, while that in the region② was dense and flat. The average electrolytic current density in the region① was initially 3×10³Am⁻² and increased with time, while that in the region② was initially 1×10²Am⁻² and decreased gradually for hours.

The morphology did not depend critically on Na₃TiF₆ concentration though its solubility seemed to be low at 673K. On the other hand, the morphology changed with time. The samples ②-a and ②-b in Fig.4 have different morphologies though both were obtained in the region②.

Typical change in the electrolytic current in the region② with time was shown in Fig.5. After the rapid attainment of double layer current, the current decreased gradually with time. The current reached minimum Iₘᵡ after dozens of hours, and increased gradually with time. The electrodeposits before Iₘᵡ was always flat like a sample②-a in Fig.4, while that after Iₘᵡ was irregular like a sample②-b. The current increase after Iₘᵡ should be caused by the increase in active surface area. The time length of Iₘᵡ depended on other electrolysis conditions, and the flat and dense deposit layer up to 50μm thickness was obtained under suitable conditions.

The behavior in NaF-NaBF₄-Na₃TiF₆ system is similar to that in NaF-NaBF₄-Na₂TiF₆ system. The electrodeposits were obtained by constant-potential electrolysis at the more negative potential than the peak(II'). The morphology changed with cathodic potential; Flat and dense deposit was obtained at more positive potential than that where the cathodic current increased sharply at the voltammogram, while the powdery deposit was obtained at more negative potentials.

2.2 Composition of deposit

The X-ray diffraction patterns of the electrodeposits were shown in Fig.6. The TiB₂ peaks and some minor peaks which did not agree with the peaks of Ti, Ni and other titanium boride

![Fig.5 Change in electrolytic current with time.](image)

![Fig.4 SEM images of surface and cross section of typical electrodeposits on Ni plate.](image)
were found in the patterns of sample-a (2-a in Fig.4). The TiB₂ peaks and the Na₂TiF₆ peaks were found in the pattern of sample-b (2-b in Fig.4). The surface of sample-b was irregular and many voids existed as shown in Fig.4, and Na₂TiF₆ which was synthesized as an intermediate element should remain in the recess of these voids.

It was reported that Ti(II) ion was unstable whereas Ti(III) ion was stable in fluoride melt(9). The result of voltammetry in NaF-NaBF₄-Na₂TiF₆ system showed that Ti(III) ion existed as an intermediate element, and Na₂TiF₆ was detected in some electrodeposits. These results confirmed that Ti(III) ion in this system was as stable as in other fluoride melts. The element of Ti(II), such as Na₂TiF₆, was not detected in an electrodeposit. Ti(II) ion might exist just as an intermediate element.

The quantitative measurement of B was difficult because of its small atomic number and the characteristic as semi-metal. There is not a proper method to measure the B content in electrodeposits since its amount in this study was usually very small and the surface was often irregular.

Only Ti and B were qualitatively detected as major elements by EPMA. The quantitative results by EPMA of the electrodeposits and TiB₂ powder(Kishida Chem., reagent grade) were shown in Table 1 though B could not be measured quantitatively. The values were not normalized to unity. The Ti content in electrodeposits was in good agreement with that in TiB₂ reagent. Considering the theoretical Ti content in TiB₂, 68.9 mass%, and characteristic difference of TiB₂ from Ti metal, the electrodeposits was concluded to be TiB₂.

2-3. Current efficiency

The results of EPMA and XRD showed that the main ingredient of electrodeposits was TiB₂. Therefore the total cathodic reaction should be assumed as follows:

\[
\text{Na}_2\text{TiF}_6 + 2\text{NaBF}_4 + 10\text{e}^- \rightarrow \text{TiB}_2 + 4\text{NaF} + 10\text{F}^- \tag{3}
\]

The current efficiencies were estimated with the weight change in electrode and the amount of electricity, though the significant figure was limited by the accuracy of weight measurement. The estimated values were 80~90% for the flat deposits, while the excesses exceeded 100% for the dendritic deposits. This might be because melt components or Ti compound, such as Na₂TiF₆, remained in the dendritic deposit.

2-4. Dependence on substrate

TiB₂ was also electrodeposited on Fe electrode in NaF-NaBF₄-Na₂TiF₆ system, and the flat, dense and adhesive layer was obtained under suitable conditions. However, the thickness was usually a few microns and the thick layer more than 10μm has not been obtained yet. The time length of morphology change on the Fe substrate might be shorter than that on Ni.

IV Conclusion

In NaF-NaBF₄ with titanium fluoride, the adhesive TiB₂ deposit was obtained at more negative potentials than that of the reduction of Ti(III) → Ti(II). The morphology depended on the electrolytic potential and the time length of electrolysis. The flat TiB₂ electrodeposit was obtained under the conditions as follows;

1) The cathode potential had to keep more positive than the potential where the cathodic current began to increase sharply in a voltammogram. The electrolytic current was relatively low, and decreased gradually in this region

2) The electrolysis had to be stopped before the electrolytic current began to increase. Therefore the monitoring of current should be important to obtain the electrodeposits with good morphology.

The dependence of morphology on Ti ion concentration and on substrate was not critical, and the flat and dense TiB₂ layer was deposited on Fe electrode.

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Reference